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Adding tracer can reduce effectiveness of acephate

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To assess the coverage of a chemical spray, a tracer is often added to an insecticide. When ferric chloride was added to acephate (Orthene 75S) to serve as the tracer, a precipitate formed and gray, washed-out spots appeared on the assessment cards set out in the experimental area. Laboratory analysis showed that when ferric chloride was added, up to 10 percent of acephate was removed, thereby weakening the effectiveness of the spray. For effective field coverage, the compound should be sprayed as soon as the ferric chloride is added. If the time between mixing and actual spraying cannot be controlled, uncertainties will exist as to the actual amount sprayed.

Oxford: 414.12–015.3 Orthene 75S
Retrieval Terms: Insecticides; organophosphates; Orthene 75S; field evaluation; tracers; chemical tracers; ferric chloride; acephate.

Use of chemical insecticides is one of the several tools available to the forest manager in combating insect pests. In applying these chemicals, the manager needs the most effective spray technique—the right dose at the right time applied to the target insects. This strategy requires that (a) the exact amount to be sprayed must be known; (b) the insecticide will not clog the nozzles of the sprayers; (c) the area where the spray landed must be known; and (d) the chemical meets the standards for environmental safety.

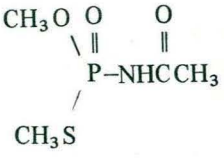
Orthene 75S (acephate) is currently undergoing field evaluation for use in control of a variety of forest insect pests, including western spruce budworm, Douglas-fir tussock moth, and southern pine beetle. To evaluate the qualities of this compound, chemically treated cards are placed in experimental plots before spraying to detect spread, particle sizes, and air drifts of spray droplets. A chemical tracer is used to detect amount of spray deposited.

In a field test of Orthene 75S in a water-based formulation, ferric chloride was used as a tracer material in conjunction with the tannic acid-impregnated cards.[1] Some workers reported[2] that when ferric chloride was added to the solution, a precipitate formed. Moreover, gray, washed-out spots were noticed on the assessment cards where the formulation landed instead of the black, distinct spots produced by ferric chloride alone on tannic acid treated cards. It seemed possible that the precipitate might clog the nozzles of the sprayers and that the ferric chloride might be reacting in a way not anticipated. Because of these concerns, several questions were raised as to the suitability of using ferric chloride as a tracer material in Orthene: (1) Is the ferric chloride detrimental to the Orthene spray? (2) Will the precipitate that forms clog the spray nozzle? (3) Does the reaction of the ferric chloride with Orthene influence spray effectiveness? and (4) What is the nature of the ferric chloride-Orthene compound, if it is formed?

To answer these questions I did a laboratory analysis of ferric chloride in Orthene 75S. The results suggest that the addition of ferric chloride to Orthene spray formulation removes three equivalents of Orthene for each equivalent of ferric chloride added. This results in removal of up to 10 percent of the Orthene, thereby weakening its effectiveness. The formulation should be sprayed as soon as the ferric chloride is added so that it will not clog the nozzles of the sprayers. Otherwise, where time between mixing and actual spraying is a somewhat uncontrollable factor, uncertainties will exist as to the actual amount of Orthene sprayed.

LABORATORY ANALYSIS

Acephate (Orthene 75S) is an organophosphate insecticide with acetyl phosphoramidothionic acid *O, S*-dimethyl ester as its active ingredient (1):



(1)

Addition of 0.2 percent (wt/vol) ferric chloride hexahydrate to a formulation of 0.5 lb Orthene 75S per gallon in water is the experimental spray dosage recommended by the manufacturer.

METHODS AND MATERIALS

Except for one run with analytical grade (99.5 percent) Orthene, commercial grade Orthene 75S was used throughout the study. Other chemicals were reagent grade materials purchased from laboratory suppliers. Iron was determined by edetic acid (EDTA) titration.[3] Infrared spectra were determined with a Perkin-Elmer 336 spectrophotometer.

Iron Salt from Field Formulation

A mixture of 0.2 g ferric chloride hexahydrate and 6.0 g Orthene 75S in 100 ml water was agitated for 24 hours. The precipitate that formed was filtered on a coarse sintered glass filter, washed with water, and dried.

Iron Salt from Equimolar Reaction

A solution of 0.10 g (0.5 mmole) Orthene (99.5 percent), 0.14 g (0.5 mmole) ferric chloride hexahydrate, and 2.5 ml water was stirred at room temperature for 3 days. The precipitate was collected, washed, and dried to yield 0.06 g of a white solid. The compound contained no chlorine as shown by the Beilstein and silver nitrate tests.[4] The amount of iron found by titration was from 6 to 10 percent; the calculated iron percentage for a 1:1 Orthene-iron compound is 20.4 percent, and for a 3:1 Orthene-iron compound is 9.2 percent.

Methylation of Iron Salt

A mixture of 0.12 g iron salt from the first reaction and 0.16 g methylmethanesulfonate in 15 ml acetonitrile was stirred at room temperature overnight. The solution was analyzed by two-dimensional thin-layer chromatography using silica gel G plates (Camag 30079) with acetonitrile first and 1:1 ratio of cyclohexane and acetone second. Phosphorus material was detected using the Watt's method.[5]

RESULTS

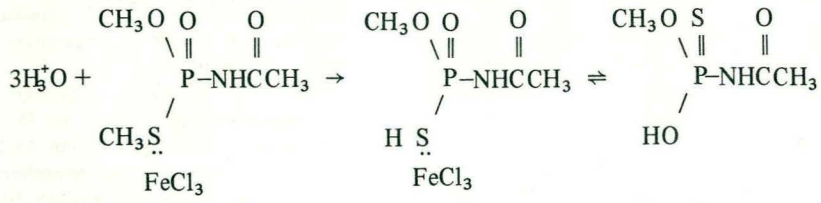
At the concentrations tested, ferric chloride reacts immediately upon its addition to a water solution of Orthene. The reaction is noted by the clouding of an otherwise clear solution. It proceeds slowly over a period of from 1 to 3 days, and continues to form precipitate. If, after the addition of ferric chloride, agitation is maintained throughout the period, the precipitate that forms is finely divided and is slightly soluble in water. Iron ions are detected by the Prussian blue color of the water solution of the precipitate. The pH of an 0.2 percent solution of ferric chloride is in the range of 3.0 to 3.5, whereas the pH of 0.5 lb Orthene 75S in a gallon of water is in the range of 4.0 to 4.5. Infrared spectrometry showed that the iron salt from the field formulation and the salt from analytical grade Orthene are identical. Methylation of the iron salt gave only one phosphorus-containing compound, which was co-chromatographable with acetyl phosphoramidothionic acid *O,O*-dimethyl ester (Ortho 14071 = 2).[6]

DISCUSSION

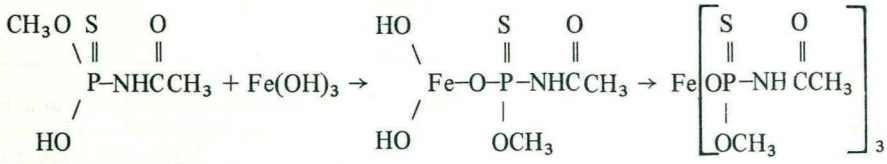
The reaction of ferric chloride with Orthene in water appears to be a two-step reaction; the first step is catalyzed by the acidity of the solution. Orthene is first hydrolyzed by the ionized ferric chloride (Eq. 1 and 2). This step is followed immediately by the formation of the primary, then secondary, and finally tertiary, salt of Orthene with ferric ion (Eq. 3).

(Eq. 1) $FeCl_3 + 6H_2O \rightarrow Fe(OH)_3 + 3H_3^+O + 3Cl^-$

(Eq. 2)

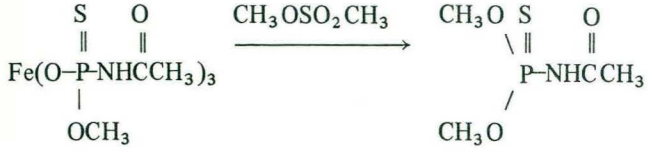


(Eq. 3)



Since hydrolysis of the methyl-thio bond is unlikely before the hydrolysis of the P-N and methyl-oxy bonds, ferric ions must be involved in the hydrolysis. One hypothesis is that a ferric ion is coordinated with the unshared electrons of the sulfur, thus weakening the methyl-thio bond for subsequent hydrolysis (Eq. 2). From the iron analysis, the results of methylation to acetyl phosphoramidothionic acid *O,O*-dimethyl ester (Eq. 4), and comparison of the known S-sodio salt of Orthene (iron salt has no P→O doublet at 1150 cm^{-1}, has P→S at 600 cm^{-1}) by infrared spectrometry,[6] the structure of the iron salt of Orthene is postulated as (3) in Equation 4.

(Eq. 4)



(3) (2)

CONCLUSIONS

The addition of ferric chloride to Orthene spray formulation is detrimental to the extent of removing 3 equivalents of Orthene for each equivalent of ferric chloride added–0.2 percent to 0.5 lb Orthene 75S per gallon spray will remove up to 10 percent of the Orthene. Since the secondary and tertiary iron salts appear to form slowly after the initial and rapid primary salt formation, it is imperative to use the formulation as soon as the ferric chloride is added. Because the ferric chloride is complexed by Orthene in the spray, the normal black compound formation with tannic acid will be washed out. The salt formation will probably be fine enough, if adequate agitation is maintained, so that it will not clog spray nozzles. In actual field experimental or operational usage, if the time between the mixing of the ferric chloride with the insecticide and the actual spraying cannot be controlled, uncertainties will exist as to the actual amount of Orthene sprayed. This is because of the slow destruction of Orthene by ferric chloride. Moreover, the intensities of the color spots on the assessment cards will vary, being less intense if there is a delay in spraying.

NOTES

[1] Maksymiuk, Bohdan. 1976. *Study on the effect of ferric chloride on insecticidal activity of* Bacillus thuringiensis *and Orthene to the Douglas-fir tussock moth.* Unpublished Report on file, 20 p. Pacific Northwest Forest and Range Exp. Stn., Corvallis, Oregon.

[2] Personal communication from George P. Markin, Pacific Southwest Forest and Range Exp. Stn., Davis, California, to Donald Curtis, Southern Region, Forest Service, May 2, 1977.

[3] Wilson, Cecil L., and David W. Wilson. *Comprehensive analytical chemistry.* IB:288. Elsevier, Amsterdam.

[4] Hazzard, B. J. 1973. *Organicum.* p. 611-612. Addison-Wesley, Reading, Mass.

[5] Watts, R. R. 1965. *4-(p-Nitrobenzyl)pyridine, a new chromagenic spray reagent for the organophosphate pesticide.* J. Assoc. Off. Agric. Chem. 48:1161.

[6] S-Sodio O-methyl acetyl phosphoramidothioate and Ortho 14071 were furnished through the courtesy of Chevron Chemical Company, Richmond, California 94804.

The Author

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